

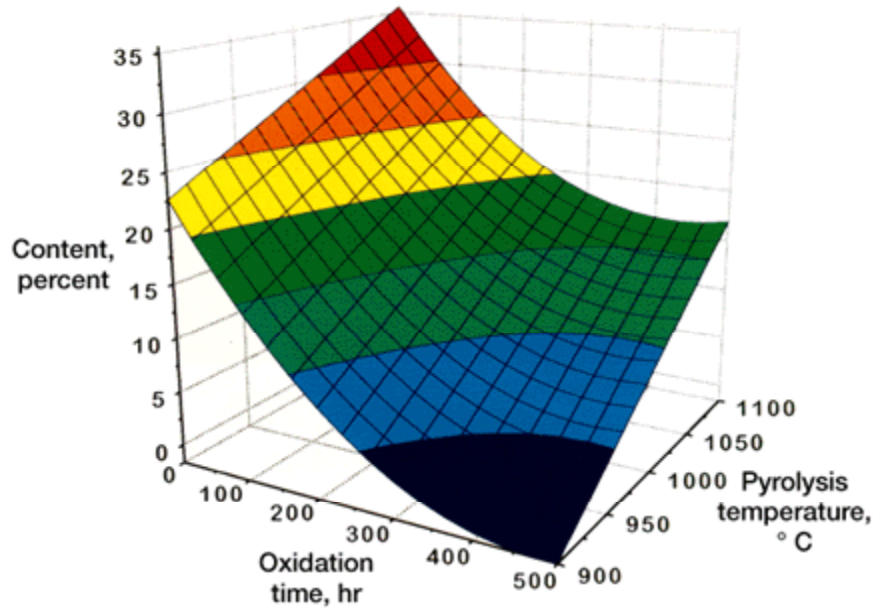
Nuclear Magnetic Resonance Used to Quantify the Effect of Pyrolysis Conditions on the Oxidative Stability of Silicon Oxycarbide Ceramics

This work was undertaken in support of the Low Cost Ceramic Composite Virtual Company, (LC³), whose members include Northrop Grumman Corporation, AlliedSignal Inc., and Allison Advanced Development Company. LC³ is a cost-shared effort funded by the Advanced Research Projects Agency (ARPA) and the LC³ participants to develop a low-cost fabrication methodology for manufacturing ceramic matrix composite structural components. The program, which is being administered by the U.S. Air Force Wright Laboratory Materials Directorate, is focused on demonstrating a ceramic matrix composite turbine seal for a regional aircraft engine. This part is to be fabricated by resin transfer molding of a siloxane polymer into a fiber preform that will be transformed into a ceramic by pyrolytic conversion.

Pyrolysis conditions are known to have a profound effect on the silicon redistribution reactions involved in converting the polymer into a ceramic (refs. 1 and 2). Different relative amounts of silicon carbide, silicon oxide, and silicon oxycarbides are produced, depending on the structure of the starting polymer and the pyrolysis path. These variations directly affect the oxidative stability. The purpose of this study was to quantify the effect of pyrolysis variables, namely time and temperature, on the redistribution reactions and, hence, on the oxidative stability.

Solid sample ²⁹Si nuclear magnetic resonance spectroscopy (NMR) can distinguish between various silicon species. For that reason, ²⁹Si NMR was used in this study to directly measure the percent peak areas of silicon carbide, silicon oxide, and silicon oxycarbides in ceramic test samples. Samples were produced under different pyrolysis conditions and were analyzed both before and after oxidation for 500 °hr at 600 °C. The pyrolysis temperature was varied between 900 and 1100 °C, and the pyrolysis time was varied from 1 to 5 hr.

Ceramic samples were prepared by AlliedSignal and analyzed by NMR at the NASA Lewis Research Center. The experiments were carried out under a statistical design in a randomized run order. In this way, the data could be analyzed by multiple linear least squares regression to give models predicting the effect of the variables on the NMR peak areas. A three-dimensional graph of the predictive model for percent silicon carbide peak plotted versus pyrolysis temperature and oxidation time is shown. Color bands represent silicon carbide contours in 5-percent intervals. This graph clearly demonstrates that increasing pyrolysis temperature significantly increases the amount of silicon carbide produced during pyrolysis. This increased silicon carbide production greatly improved oxidative stability, as evidenced by the greater retention of silicon carbide after oxidation. Pyrolysis time had little effect on percent silicon carbide.



Predictive model for percent silicon carbide peak area plotted versus pyrolysis temperature and oxidation time.

We concluded that pyrolysis at 1100 °C produces the most oxidatively stable ceramic matrix. Furthermore, for samples like these with large surface-to-volume ratios, there is no benefit in pyrolyzing for more than 1 hr. Shorter pyrolysis cycles can greatly reduce the cost of producing the ceramic part.

References

1. Hurwitz, F.I., et al.: Characterization of the Pyrolytic Conversion of Polysilsesquioxanes to Silicon Oxycarbides. J. Mater. Sci., vol. 28, 1993, pp. 6622-6630.
2. Hurwitz, F.I.; Heimann, P.J.; and Kacik, T.A.: Redistribution Reactions in BlackglasTM During Pyrolysis and Their Effect on Oxidative Stability. Ceram. Eng. and Sci. Proc., vol. 16, no. 4, 1995, pp. 217-224.